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PATENT SPECIFICATION

DRAWINGS ATTACHED

1,080,649

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COMPLETE SPECIFICATION

Method to increase Adhesion of a Polyolefin Coating to Substrates

We, NATIONAL DISTILLERS AND CHEMICAL CORPORATION, a Corporation organised and existing under the laws of the State of Virginia, United States of America, of 99 Park Avenue, New York 16, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for rendering a substrate adherent to a polyolefin coating applied thereto or thereon by extrusion.

The application of polyethylene to substrates by the extrusion coating technique has resulted in a wide range of new packaging materials. The main purpose of coating a substrate with a polyolefin is to combine the properties of the two materials. Contributions of the polyolefin coating include a heat-sealable surface, increased tear and crease resistance, and a barrier against grease, oil, and moisture. For example, some of the applications in which polyethylene-coated substrates are being used are bags and cartons for packaging foods, chemicals, fertilizers, and resins, vacuum-forming materials for packaging, construction materials, military packaging, and decorative finishes.

Polyethylene is coated to the substrate by extruding a thin curtain of molten resin onto the surface of the substrate and thereafter pressing it against or into the substrate, or both, with or without the use of chemical primer on the substrate. The effectiveness of the coating is largely dependant upon the adhesive bond established between the polyethylene coating and the substrate. Polyethylene coatings exhibit some degree of

natural adhesion to some substrates, e.g., most paper and paper board, because both chemical and mechanical forces contribute to the bond strength. On the other hand, polyethylene coatings exhibit substantially no natural adhesion to crystalline polypropylene and polystyrene substrates. In turn, the strength of this bond is affected by the rate at which the coating is applied, increasing coating speeds leading to decreasing adhesion of the coating. For example, in spite of the fact that chemical and mechanical forces are favorable to the formation of a bond of polyethylene to porous substrates such as paper and paper board, the strength of such a bond is still so weak that it severely limits the speed at which the polyethylene coating can be applied.

Several methods have been proposed for rendering the surfaces of polyethylene substrates more receptive to coatings of laminating adhesives. For example, G. W. Traver, in a patent filed prior to the discovery of crystalline polypropylene (U.S. Patent Specification No. 3,018,189) broadly disclosed an electronic treatment to render the surface of polyethylene films more receptive to adhesives applied to bond such films in a sandwich or laminate structure. In a patent filed subsequent to the discovery of crystalline polypropylene, Hirt (U.S. Patent Specification No. 2,998,324) points out that treatments adequate to render the surface of polyethylene adherent to "lacquers, enamels, and similar coating compositions", e.g., heat and flame treatment, chemical treatment, or electronic treatment, are not effective by themselves in rendering the surface of crystalline polypropylene adherent to such coatings. Instead, Hirt indicates that the coating of crystalline polypropylene requires a multistep procedure that includes the appli-

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cation of specific combinations of compatible primers and top coats. Accordingly, Traver's process cannot be extrapolated to polyolefin substrates other than polyethylene. Further, 5 neither Traver nor Hirt teaches the application of a polyolefin coating to a polyolefin substrate, e.g., polypropylene or polystyrene, or to non-plastic substrates, e.g., paper and paper board.

10 In accordance with the present invention there is provided a method of treating the surface of a substrate to improve the adherence of the surface to a subsequently applied extrusion coating of a polyolefin plastics material, the method comprising subjecting the surface to the action of a corona discharge at a voltage of 10,000 to 25,000 volts from an electrode spaced from .025 to .25 inch away from the surface, the substrate being advanced past the electrode at a speed of 200 to 600 feet per minute.

15 The term "polyolefin" employed herein refers to any polymerised olefinically unsaturated hydrocarbon, and in particular includes polystyrene.

20 Corona discharge treatment of materials of the character with which the present invention is concerned requires the production of a controllable corona discharge at the surface of the substrate being treated.

25 In general, a suitable device or apparatus includes an alternating electrical current source to provide a high voltage and high frequency current to an electrode upon which the corona discharge is generated, a grounded 30 back-up member which, conveniently, is a roller and serves to complete the electrical circuit, and a dielectric member which is interposed between the electrode and the back-up member and which functions to spread the corona discharge along the length of the electrode.

35 The substrate being treated is advanced longitudinally beneath the electrode (or electrodes) while corona is being discharged therefrom. Further, a buffer dielectric member is normally present to prevent concentration 40 of corona discharge at a pinhole or other defect in the substrate to obviate burning or otherwise damaging of the substrate at the area of such defect. This buffer dielectric layer may be positioned adjacent to the electrode or back-up member, as desired.

45 Any suitable electrode means for providing the electrostatic accumulation and discharge of electrons may be used. Examples 50 are the helical knife edge type or the tubular gaseous conduction lamps, as well as others such as tubes, rods, screens, plates, or others.

55 For purposes of illustration, embodiments 60 of the invention will now be described with reference to the accompanying drawing wherein:

65 Fig. 1 is a side view in elevation of apparatus for treating substrates in accord-

ance with the present invention;

Fig. 2 is a perspective plan view of apparatus for carrying out the invention on a flexible sheet of substrate.

70 In the illustration given in Figs. 1 and 2, the substrate to be treated is in the form of a flexible web such as kraft paper, polypropylene film or sheet. The web 2 is drawn from a supply roll 1 around a guide roll 4 under a tension adjusted by the pressure of the pressure roll 3 against the guide roll 4. The web is then led around idler rolls 5 and 6 over a path 7 and 8 to the treater roll 9. Where heating of the substrate is desired prior to the coating thereof, for example for the purpose of removing undesirable moisture from the substrate, suitable heating means, such as heated rolls (not shown), may be interposed between roll 5 and the treater roll 9. Substrate temperature, as long as it does not affect the physical properties of the substrate web, does not interfere with the electronic treatment of this invention.

75 The treater roll 9 is an insulated, grounded, metal roll. It serves to complete the electrical circuit emanating from the electrode 10 to which a high voltage and high frequency electric current is supplied from an alternating current source 10a and upon which electrode 10 the corona discharge is produced.

80 One suitable means for supplying a high voltage, high frequency current to the electrode is a spark-gap excited high frequency oscillator, such as is exemplified by a Lepel treater, Model HFSG-2, supplied by Lepel High Frequency Laboratories, Inc. In using such a unit, the current frequency is controlled by adjusting the inductance of a primary oscillating circuit to tune it with an output circuit wherein are contained the treater electrode and the treater roll. A frequency within a narrow range centering around 450 Kc. is obtainable. Intensity of treatment is controlled through regulation of the capacitance of the primary circuit whereby the current is varied. The primary current can range up to 1.5 amperes to give a treatment voltage ranging from 10,000 to 25,000 volts. Another suitable means for imparting a high voltage, high frequency current to the treater electrode is provided by a Mancib-type treater which comprises a circuit combination herein a generator is the power source, delivering a high frequency alternating current to a primary circuit, which current is stepped up to high voltage by a transformer linking the primary circuit to a secondary circuit containing the treater electrode. Current frequency generated ranges from about 500 to 17,500 cycles per second. Primary current and voltage are adjustable to give a secondary voltage at the gap between the treater electrode and the treater roll of from 10,000 to 25,000 volts

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so that a corona discharge occurs.

It is usually desirable to cover the surface of the treater roll with a wrapper 10c of a dielectric material to facilitate spreading of the corona discharge along the length of the electrode, thereby alleviating the deleterious effects from an excessive concentration of the corona discharge at a pin-hole or other defect in the substrate. A suitable dielectric covering for the treater roll is provided, for example, by three wraps of two-mil "Mylar" (Trade Mark) film.

Although a variety of suitable means exist upon which an effective corona discharge can be generated, the means shown in the drawing is a helical knife edge (threaded stud) electrode. Referring specifically to Fig. 2, this helical knife edge electrode 10 extends transversely across the width of the web being treated in close parallel relationship to the surface of treater roll 9. Such an electrode has a continuous knife edge 10b which repetitively presents a portion thereof into corona discharge spatial relationship to the treater roll, the knife edge 10b generally paralleling the direction of travel of the substrate or web being treated, this direction of travel or movement coinciding with the longitudinal axis of the web. The space at its closest between the knife edge 10b and the surface of the treater roll 9 is from 25 to 250 mils, although generally it is adjusted to within a range of 30 to 80 mils. A conventional dielectric layer 10c is interposed between the electrode 10 and the treater roll 9.

Other electrodes, for example a serrated element resembling a file or rasp, may also be satisfactorily employed. It is also possible to employ several electrode members, and these may have various lengths as required. Where multiple electrodes are employed, they are preferably arranged in parallel concentric relationship to each other and the surface of the treater roll, and are spaced apart at a distance which prevents undesirable heat build-up at the surface of the substrate from multiple corona discharges.

When energized with a high voltage and high frequency alternating current, the electrode in combination with the surface of the grounded treater roll 9 serves to establish an electrostatic field of alternating character between the treater roll and the electrode. This field produces a pulsating electrical discharge between the electrode and the treater roll surface at the frequency of the actuating energy supplied to the electrode, and the electrons thus discharged will be applied continuously to the web of substrate as it passes longitudinally along path 8 through the treatment zone formed by electrode 10 and the surface of treater roll 9. As a consequence, the surface of the substrate which faces toward the electrode and

opposite the treater roll surface is rendered highly receptive and adherent to an extruded layer of a polyethylene.

The treated substrate 11 may, if desired, be led directly from the treatment zone to a suitably positioned wind-up roll and there wound and stored for coating in a separate operation at a later time. Preferably, the treated substrate 11 is led directly through a short distance to the nip formed by a pressure roll 12 and a chill roll 17. The pressure roll 12 is a large metal idler roll with a covering of neoprene or silicone rubber. The chill roll is usually a driven, chrome-plated twin-shell steel drum cored for chilled water throughout to provide temperature control and heat transfer for the molten web during its transition from melt to solid state. Chill roll temperature is usually held between about 70° and 100°F. The polyethylene resin is fed into a hopper 13, melted by subjecting it to heat and pressure inside the extruder barrel 14, and forced by an extruder screw through the narrow slit of the extrusion die 15. The extruded melt of polyethylene 16 contacts the treated surface of the substrate at a point immediately prior to the nip formed by pressure roll 12 and chill roll 17 and thence is drawn down into the nip between the two rolls. While coming into contact with the faster moving substrate, the coating melt 16 is drawn out to the desired thickness and forced onto the substrate 11 when both layers are pressed together by the two rolls. The pressure is generally between about 50 and 100 pounds per linear inch. The combination of substrate and polyethylene 18 is then rapidly cooled by the chill roll 17. The cooled, coated substrate 19 is then pulled over a driven slitter roll 20 where it is trimmed by a pair of slitters 21 and thence led around idler rolls 22 and 23 and therefrom wrapped upon windup roll 24.

The coated substrate so obtained exhibits a heat-sealable surface, increased tear and crease resistance, and increased resistance to the passage of grease, oil and moisture.

The polyolefin substrates which may be treated according to this invention include polyolefins which exhibit virtually no natural adhesion to extruded polyethylene coatings, particularly polystyrene and crystalline polypropylene. Also suitable are other olefin polymers and copolymers, for example, ethylene-propylene copolymers, ethylene-butene copolymers, and others.

The paper substrates which may be treated according to this invention include papers derived from unregenerated cellulose and such pulps as unbleached groundwood, unbleached sulphite, bleached sulphite, unbleached sulphate, e.g., kraft, bleached sulphate, e.g., bleached kraft, neutral sulphite, and semi-kraft. Further defined by general use, paper

suitable for use in this invention includes wrapping papers, e.g., butcher's, bag, book papers, e.g., converting, lithograph, offset and text, and printing and specialty papers, e.g., bagging, catalogue, news tablet and poster. Bleached and unbleached kraft paper and paper board are particularly suitable for the practice of this invention.

It is to be understood that the term "substrate" as used herein refers in a broad sense to the foundation upon which the polyolefin coating is to be applied, whether such foundation consists wholly of a self-supporting web or whether it consists of a layer or coating upon another material.

The voltage applied to the electrode of the electronic treater should be sufficiently high relative to the dielectric value of the substrate and the air gap to bring about effective electronic bombardment and modification of the substrate surface. For the substrates included in the present invention, particularly effective treatment is obtained at voltages in the range of 10,000 to 14,000 volts.

Although polyethylene, and particularly coating grades of polyethylene ranging in density from 0.91 to 0.96 and in melt index from 1 to 12, is especially preferred as the coating for this process, it is also possible to employ other polyolefins, especially polypropylene and copolymers of ethylene or propylene with olefins, such as butene, pentene and hexene, as well as specially treated polyolefins such as chlorinated polyethylene.

For selected members of the afore-described coating grades of polyethylene and at pressures of about 50 to 100 pounds per linear inch, in-line treatment and coating speeds ranging from 50 to 1000 feet per minute or higher are possible. Coating thicknesses within the above noted ranges may

vary from as low as 0.2 mil or less up to as high as 10 to 15 mils. Generally, however, speeds of 100 to 600 feet per minute are employed in conjunction with coating thickness ranging from 0.5 to 2.5 mils.

The melt or bonding temperature depends on the characteristics of the resin used and also on the physical properties of the substrate. In general, the bonding temperature used to produce tightly adhering coatings should be the highest that is practicable, but it is limited to that at which degradation of the resin, e.g., oxidation, odour development, heat sealability, etc., occurs or becomes significant and/or at which the substrate material begins to suffer harmful effects. In the case of thermoplastic substrates, the bonding temperature must not exceed the temperature at which the substrate begins to soften. For the coating grades of polyethylene preferred by this invention, suitable bonding temperatures are achieved by extruding the polyethylene at melt temperatures ranging from 570° to 640°F., and preferably from 590° to 620°F.

It has further been found that adherence of the polyolefin coating to the substrate may improve to varying degrees during subsequent storage or aging of the coated substrate at room temperature. For example, such improvement is noticeable with kraft paper coated with polyethylene.

The following examples are presented to further illustrate, without limitation, various embodiments of this invention.

EXAMPLE I

Three polypropylenes were treated with corona discharge by a Mancib-type treater on both sides and then extrusion-coated in-line on both sides with various coating grades of polyethylene. Conditions were as follows:

TABLE I

	Run A	Run B	Run C
Polypropylene Thickness, mils	6	6	6
Line speed, ft./min.	200	200	200
Electrode voltage, volts	12,000	12,000	12,000
Dielectric (Mylar) thickness, mils	6	6	6
Distance of electrode from substrate, mils	35	47	40
Distance of electrode from coating nip, inches	32	30	33
Coating thickness (both sides), mils	1.0	1.0	1.0
Polyethylene			
Density, g./cc.	0.924	0.915	0.915
Melt index, g./10 min.	3.0	12	8
Extrusion temperature, °F.	600	600	600

5 The polyethylene coatings in each instance adhered so firmly to the polypropylene substrate that they could not be removed without rupture, this in spite of the fact that the polyethylene of Run C contained a slip additive. Control runs with untreated polypropylene produced coatings which exhibited no measurable adherence to the substrate.

10 EXAMPLE II
15 A web of 40-pound wet strength kraft paper, 15 inches wide, was transported at a rate of 200 feet per minute through the apparatus shown and therein electronically treated with a corona discharge and extrusion coated with a 1.0 mil layer of polyethylene. Electronic treatment was effected by means of a commercial treater (Model HFSG-2, Lepel High Frequency Laboratories, Inc.) by which a helically threaded knife edge electrode was positioned at a distance of 60 mils from the paper web and charged with a voltage of about 12,000 volts. The

treater roll surface was covered with three wraps of two-mil Mylar film. Treatment took place at a distance of 28 inches in front of the nip between the pressure roll and the chill roll. The polyethylene resin was a coating grade with a density of 0.924 g./cc. and a melt index of 3 g./10 min. It was extruded onto the paper at an extrusion temperature of 600°F.

25 Adhesion values of the coating were determined on the electronically treated material and, for comparative purposes, on a portion of coated substrate prepared in the same run but without electronic treatment, both "off machine" (immediate) and after an aging period of two weeks at ambient temperature. These adhesion values, listed below, 30 were determined by means of a Perkins-Southwick Bond tester (see Guillotte and MacDermot, Modern Packaging 30, No. 4, 157 (1956) and calculated in terms of per cent adhesion.

TABLE II

	Perkins-Southwick Adhesion, %	
	Off Machine	Aged 2 weeks
Treated	67	70
Untreated	31	52

WHAT WE CLAIM IS:—

1. A method of treating the surface of a substrate to improve the adherence of the surface to a subsequently applied extrusion coating of a polyolefin plastics material, the method comprising subjecting the surface to the action of a corona discharge at a voltage of 10,000 to 25,000 volts from an electrode spaced from .025 to .25 inch away from the surface, the substrate being advanced past the electrode at a speed of 200 to 600 feet per minute. 5 30

2. A method according to claim 1 wherein the substrate is treated with a corona discharge of 10,000 to 14,000 volts. 10 35

3. A method according to claim 1 or 2 whereby the substrate is a polyolefin. 15 40

4. A method according to claim 3 whereby the substrate is polypropylene or polystyrene. 20 45

5. A method according to claim 1 or 2 whereby the substrate is paper or kraft paper. 25 50

6. A method according to any of claims 1 to 3 wherein the substrate in the form of a web is passed onto a support formed of electrically conductive material with one surface of the web facing the support and the surface to be treated facing outwardly towards the electrode, corona discharge being

applied from the electrode upon the outwardly facing surface of the web and an extruded coating of a polyolefin thereafter being applied onto the treated surface of the web.

7. A method according to any of claims 1 to 6 wherein the electrode is spaced 0.03 to 0.08 inch from the surface of the substrate.

8. A method of treating the surface of a substrate to improve the adherence of the surface to a subsequently applied extrusion coating of a polyolefin plastic substantially as hereinbefore described with reference to the Examples.

9. A substrate treated by a method according to any of claims 1 to 8. 45

10. A method according to claim 6, for preparing a polyolefin substrate, substantially as hereinbefore described with reference to the Examples.

11. A polyolefin-coated substrate prepared by a method according to claim 6 or 10.

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1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

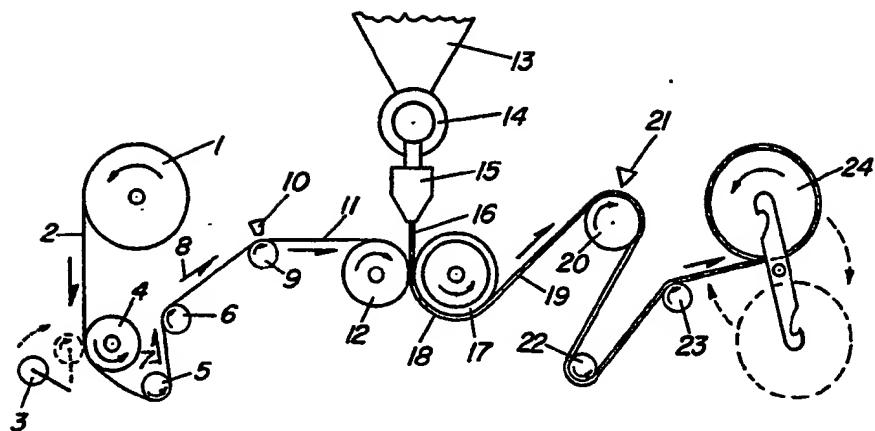


FIG. 1

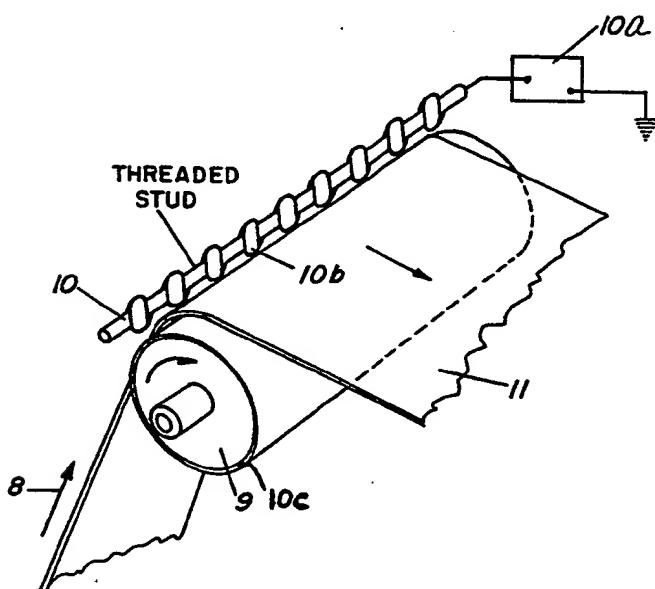


FIG. 2

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